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Photophysical processes and photochemical reactions involved in poly(*N*-vinylcarbazole) and in copolymers with carbazole units

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Abstract

This paper is devoted to the analysis of the photochemical behaviour of copolymers with carbazole units exposed to long-wavelength radiation. These copolymers are constituted of two types of carbazolylethyl methacrylate units (CEM) with octyl methacrylate moieties (OMA). The exposure of copolymers and PVK to UV light results in dramatic modifications of the physical and photophysical properties of the polymer. These modifications can be correlated with modifications of the chemical structure of the matrix. The photoageing of copolymers and PVK has been analysed by fluorescence, ESR, UV–vis and infrared spectroscopies. The effects of crosslinking and chain scissions were determined by gel fraction measurements and size exclusion chromatography.

Keywords: Poly(*N*-vinylcarbazole); Copolymers; Photophysical processes; Photochemical reactions

1. Introduction

Poly(*N*-vinylcarbazole) (PVK) has been the subject of intense photophysical study due in part to its photoconductive properties [1] and also to its unusual excimer forming characteristics [2–8]. The presence of two distinct excimer sites with typical photophysical properties is unique among vinyl aromatic polymers [5]. It has been proposed that the lower energy excimer ($\lambda_{max} \approx 420$ nm) is formed when two carbazolyl groups have achieved an eclipsed fully overlapping ''sandwich-like'' conformation [2,3]. This intrachain excimer fluorescence is common to all vinyl aromatic polymers [4]. A 120° rotation about the C–C bond of an isotactic dyad is required to bring two carbazole rings from the ground state to the excimer state where they totally overlap [2,3].

Conversely to the photophysical processes, only little attention has been devoted to the photoageing of PVK exposed to UV light at wavelengths higher than 300 nm. The light absorption by the carbazolyl group of PVK extends up to 370 nm. This makes carbazolyl moieties directly accessible to UV light of the terrestrial solar radiation. From the previous papers of Pfister and Williams [7] and Itaya et al. [8] the mechanism of phototransformation of PVK could not be considered as fully elucidated. For a better comprehension, we have focused on the analysis of the photophysical processes and photochemical reactions that are likely to occur when PVK is exposed to conditions of accelerated artificial ageing ($\lambda > 300$ nm) [9]. It is worthy to summarise the main results reported in this paper.

- The exposure of PVK to UV light, results in dramatic modifications of physical and photophysical properties of the polymer, which can be correlated with the modification of the chemical structure of the matrix. It was shown that the phototransformation of this polymer is principally governed by crosslinking reactions. A dramatic decrease of the fluorescence intensity is observed and interpreted as a reduction in the local mobility resulting from crosslinking reactions.

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- Irradiation of PVK leads also to chain scissions involving the N–C bond. Carbazolyl and macro-alkyl radicals are formed. Abstraction of hydrogen by the carbazolyl radical leads to the formation of molecular carbazole that is trapped in the irradiated film. The macro-alkyl radicals formed simultaneously may recombine, leading to crosslinking.
- The rate at which crosslinking occurs and emission decreases is largely enhanced when irradiation is carried out in the presence of oxygen. The mechanism of oxidation is quite complex as two possible pathways of photooxidation involving the carbazolyl or the aliphatic moieties can be involved:
  1. As suggested by Pfister and Williams [7], electron transfer reactions can occur in the excited state of the carbazole groups. The highly reactive O_2^- can readily form hydroperoxy type radicals ($OOH^\bullet$) that were supposed to lead to oxidation of the polymer, resulting in chain cleavage and oxidation of both the chain and the carbazole ring. The mechanism of carbazole moieties' oxidation involves the cleavage of the aromatic rings leading finally to carboxylic acid groups.
  2. Under irradiation in the presence of oxygen, primary macroradicals formed upon direct homolysis of the N–C bond are able to abstract the labile hydrogen atoms of the aliphatic units. These radicals are likely to initiate a chain oxidation by hydrogen abstraction, which is generally considered as the first step of polymer photooxidation [10].

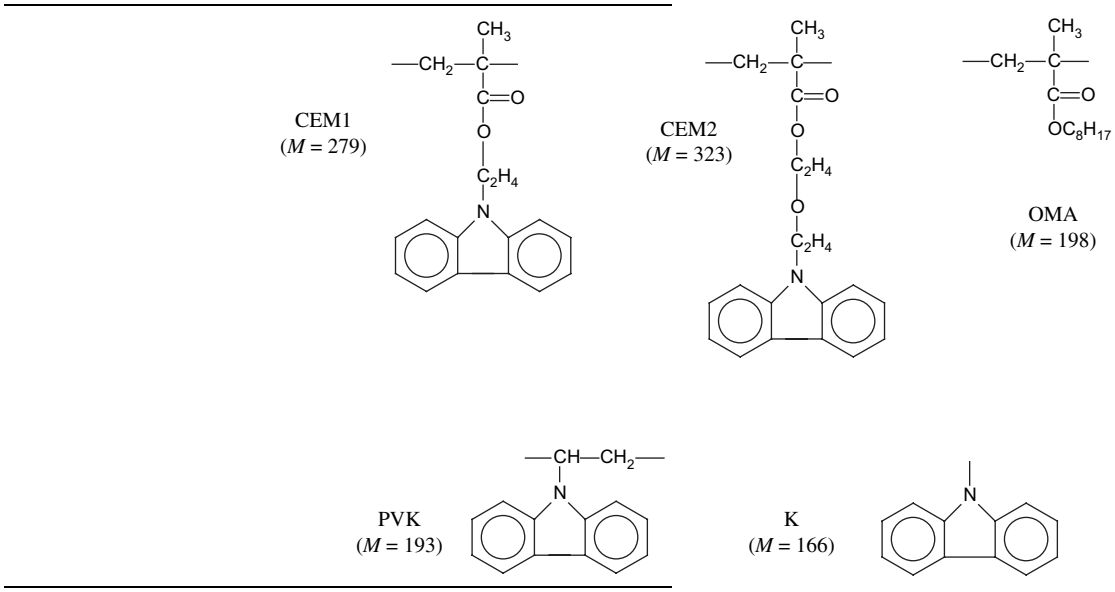
PVK is a stiff, brittle polymer with poor mechanical and processing characteristics. Copolymerisation with suitable monomers can soften the product and improve the mechanical properties of films [11]. The copolymers of PVK are promising polymeric materials for electroluminescent devices and light emitting diodes. In addition, carbazole-containing copolymers were shown to be very efficient for optical information recording [12] whilst holograms recorded in PVK are not stable. Synthesis of carbazole-containing polymers was also achieved to study the photo-properties of polymers containing the carbazole chromophore [13,14]. The aim was to determine how the properties (excimer formation and energy migration) were affected by the geometry of the attachment of the chromophore to the chain backbone. Only little attention was focused on the photochemical degradation of these copolymers. Basic molecular weight characterisation by combining membrane osmotic pressure measurement with gel permeation chromatography suggested that irradiation causes chain scission; a loss of carbazole chromophore fluorescence was also observed [14]. No chemical analysis was then carried out to elucidate the degradation mechanism.

Carbazolyl substituted methacrylate copolymers, in which the carbazolyl chromophore is attached to the backbone by a spacing group, were synthesised [15]. This work presents preliminary results on the photochemical behaviour of three copolymers of PVK with two types of carbazolylethyl methacrylate (CEM) and octyl methacrylate (OMA) in conditions of accelerated artificial ageing ($\lambda > 300$ nm). The photochemical behaviour of the three copolymers was compared to the one of PVK in terms of evolution of the chemical structure and modification of physical and photophysical properties. The influence of the chemical structure of the copolymer on the rate and on the mechanism of photodegradation has been analysed by fluorescence, ESR, UV–vis and infrared spectroscopies. The effects of crosslinking and chain scissions were determined by gel fraction measurements and size exclusion chromatography (SEC).

2. Experimental

PVK powder containing no stabilisers or additives was obtained from Aldrich.

The structures of the copolymers that were synthesised are detailed in another paper [15]. Three different compositions of copolymers containing two types of carbazolylethyl methacrylate units (CEM1 and CEM2) with octyl methacrylate moieties (OMA) were used for the investigations. The specifications of the copolymers (mol%), the molar weight of a repetition unit (M) and the percentage of carbazolic group (K%) are given in Table 1.



Copolymers were synthesised in small quantities and analyses of COPa and COPc photodegradation were therefore limited to UV–vis and infrared spectroscopies.

Thin polymer films were obtained by evaporating dichloromethane solutions on KBr plates.

Irradiations were carried out at a temperature of 30 °C in a SEPAP 14.24 unit equipped with a medium-pressure mercury lamp. This medium-accelerated photoageing device has been described previously [9]. Photooxidation corresponds to exposure in the presence of oxygen (ventilated ambient air) and photolysis corresponds to vacuum exposure. In the case of the photolysis experiments, the samples were sealed in a Pyrex tube under a vacuum of 10^{-6} Torr obtained using mercury or oil diffusion vacuum lines.

The UV–vis and infrared spectra were recorded, respectively, on a Shimadzu UV-2101 PC spectrophotometer equipped with an integrating sphere and Nicolet Magna-IR 760 FTIR spectrophotometer.

Irradiated films were exposed to reactive NH_3 (Ucar) gases at room temperature in all-Teflon reactors. Coupling the IR analysis with chemical derivatisation reactions allows an in situ identification of the carboxylic acids and esters [16,17].

The fluorescence spectra were obtained using a Perkin–Elmer LS 55 spectrofluorimeter. The excitation and emission slits were, respectively, 6 and 4 nm. The excitation wavelength was 340 nm. For fluorescence measurements thin films were deposited on glass plates using a Cookson SCS G3P8 spin coater. The thickness of the films was chosen so that the absorbance at 340 nm is 0.3.

ESR spectra were obtained with a Brücker spectrophotometer at the frequency of 9639 GHz. About 10 mg of polymer was placed in a quartz tube. The installation allows a simultaneous exposure of sample to UV radiation at $\lambda > 350$ nm.

Crosslinking of samples was evaluated by gravimetric measurements of the gel fraction. Irradiated films (about 5 mg) were immersed in tetrahydrofuran (5 mL) for 48 h. The solutions were then Büchner filtered. The insoluble fractions were dried and then weighed. Average molecular weights (Mw) of the soluble fraction of polymeric samples were obtained by universal size exclusion chromatography (SEC). SEC was carried out on a Viskotek TriSek model 270 Dual Detector using a GMH_x 7.8 mm ID column. The mobile phase was tetrahydrofuran with a flow rate of 0.8 ml/min. The calibration was achieved using polystyrene standards.

Table 1
Designation of the copolymers used in this study (mol%), molar weight (M, mol g^{-1}) of a repetition unit and percentage of carbazolic group (K%) in each polymer

Polymer	CEM1 (%)	CEM2 (%)	OMA (%)	M	K (%)
COPa	80	–	20	262.8	50.5
COPb	30	30	40	259.8	38.3
COPc	40	40	20	280.4	47.4
PVK				193.0	86.0

3. Results and discussion

3.1. Evolution of the chemical structure

It was shown that the photodegradation of PVK is limited to the first 20–30 μm of the film due to the acute profile of light absorption by the carbazolyl groups in the near UV range [9]. For a comparison purpose, PVK and copolymer samples were prepared so that all of them have the same absorbance relative to the carbazolyl moieties (the carbazolyl content was estimated from the intensity of the ring vibration at 1596 cm^{-1}). The concentration of carbazolyl groups in each polymer is reported in Table 1.

In order to obtain the same absorbance, we prepared films with different thickness varying in the following order: PVK (15 μm) < COPa < COPc < COPb. Consequently, the comparison of the degradation curves will need to be carefully interpreted. Usually, the degradation rate of a polymer is characterised by the measurement of the concentration of the stable photoproducts detected by UV–vis and infrared analyses. The photo-yellowing can be evaluated by measuring the increase of absorbance at 400 nm. Measuring the increase of absorbance in the infrared domain can be used to characterise accurately the progress of the photooxidation reactions. The concentration (c) of IR or UV–visible absorbing products is linked to the absorbance according to the Beer–Lambert's law:

$$\text{Absorbance} = \varepsilon \times c \times l$$

where ε = molar absorption coefficient and l = thickness of the irradiated film.

For IR and UV analyses of photoageing, two types of irradiation were carried out: vacuum exposure (photolysis) to point out the modification of the chemical structure of the matrix without involvement of oxygen, and irradiation at ambient air (photooxidation).

Under photolysis conditions, the development of an unstructured absorption above 370 nm on the UV–visible spectra of irradiated samples was observed. The increase of absorbance at wavelengths higher than 400 nm was fairly weak and no significant discoloration was observed after photolysis.

Irradiation of copolymers and PVK at ambient air leads to much more important changes of the UV–visible spectra. A large increase of absorbance in the range of 300–500 nm is observed and corresponds to the yellowing of the samples.

The variations of absorbance at 400 nm for copolymers and PVK as a function of UV irradiation in the absence and in the presence of oxygen are presented in Fig. 1.

The kinetic curves in Fig. 1 show that the tendency towards discoloration is higher in PVK than in copolymers, under both conditions of exposure. It can be recalled that an increase of absorbance in the visible domain is related to the formation of conjugated species. A plausible explanation of our results is that spacing the carbazolic units by CEM and OMA

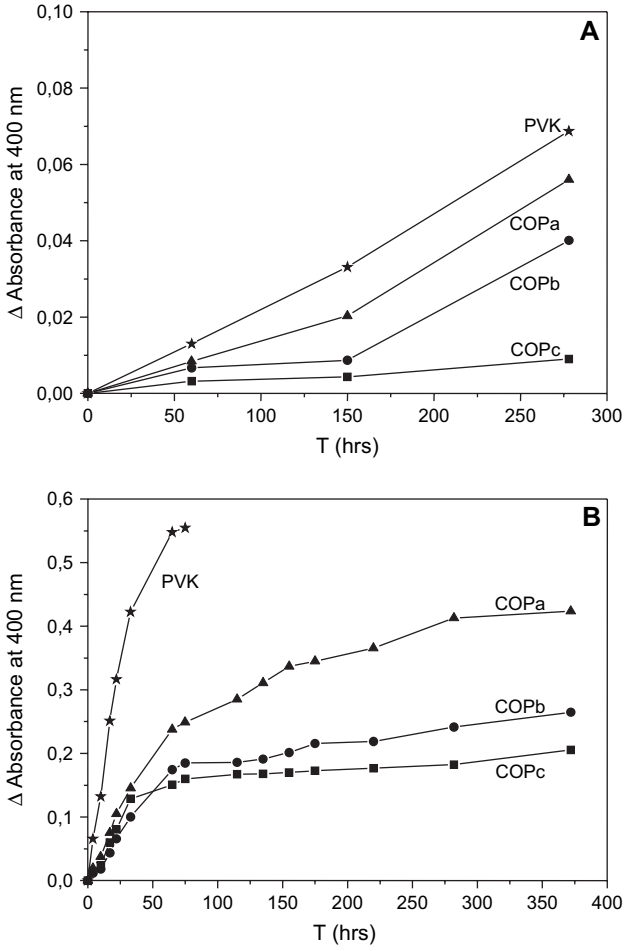


Fig. 1. Increase of absorbance at 400 nm of PVK and copolymers irradiated in the absence (A) and in the presence (B) of oxygen in the SEPAP 14.24 unit at 30 °C.

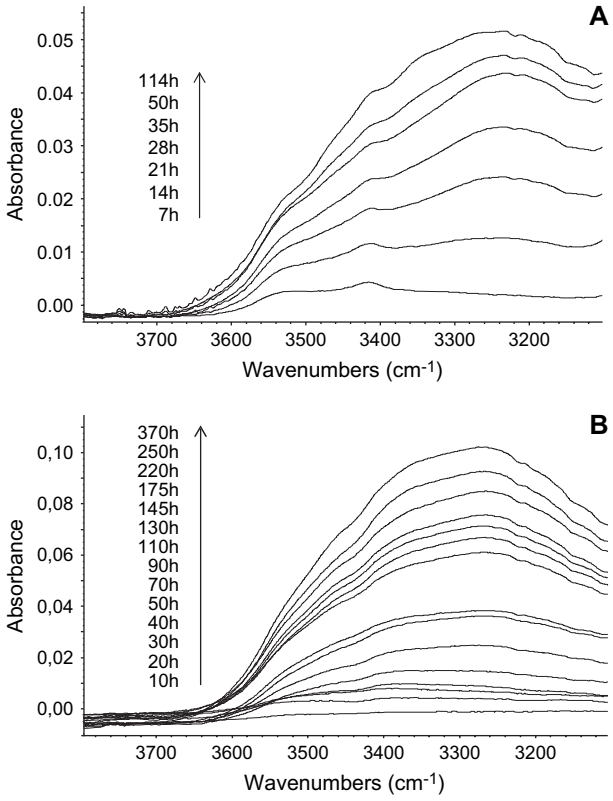


Fig. 2. Changes in the 3800–3100 cm^{-1} region of the IR spectra (subtraction between the irradiated and the non-irradiated sample) of PVK (A) and COP film (B) caused by photooxidation in the SEPAP 14.24 unit at 30 °C.

moieties inhibits the extension of conjugation between carbazolyl units.

Concerning the copolymers, the decreasing order – COPa > COPb > COPc – will be discussed after infrared analysis.

The photooxidation of copolymers and PVK leads to dramatic modifications of the IR spectra, which can be observed in the 3800–3100 cm^{-1} region and in the 1900–1550 cm^{-1} region. The ester function in copolymers results in the presence of a broad ν(CO) band centred at 1735 cm^{-1} with a harmonic band at 3430 cm^{-1} on the IR spectra before exposure. These initial absorption bands make the analysis of the spectral modifications of copolymer rather difficult. However, the subtraction of the initial spectrum before oxidation to the spectra recorded after several oxidation times allows the observation of several maxima that are formed in the carbonyl and hydroxyl domains.

In the 3800–3100 cm^{-1} region (Fig. 2A), the formation of an absorption band is observed with several maxima at 3511 cm^{-1} (free alcohols and hydroperoxides groups), 3417 cm^{-1} (N–H vibration) and around 3230 cm^{-1} (associated OH groups of acids) [9]. The broad band centred around 3230 cm^{-1} becomes pre-eminent as irradiation proceeds. Such an evolution, which is classically observed in the photooxidation of aromatic polymers, can be attributed to the accumulation of carboxylic acid groups.

In the case of copolymers (Fig. 2B), one can observe the appearance of a broad absorbance centred at 3230 cm^{-1} with a shoulder around 3500 cm^{-1}, which, respectively, accounts for the formation of acids and alcohols. The decrease of the intensity of the initial band at 3430 cm^{-1} prevents from observing the N–H absorption band at 3411 cm^{-1} as observed in PVK.

In the 1900–1550 cm^{-1} region (Fig. 3A), photooxidation of PVK leads to the formation of a band with several maxima or shoulders at 1835, 1770, 1728, 1687 and 1655 cm^{-1}. As irradiation proceeds, the maximum at 1728 cm^{-1} shifts progressively to 1715 cm^{-1}. The development of a thin band at 1610 cm^{-1}, located between two polymer ring vibrations at 1626 and 1597 cm^{-1}, the intensity of which decreases, is due to the modification in ring substitution.

In the case of copolymer, the strong initial band between 1750 cm^{-1} and 1700 cm^{-1} arising from the C=O stretching vibration of the ester function is enlarged at both extremities. A mask has been inserted (Fig. 3B) in the zone of the high initial absorbance of ester groups where the subtraction is impossible. As a result, an increase of the absorbance in the regions 1850–1750 cm^{-1} and 1700–1550 cm^{-1} is observed. A

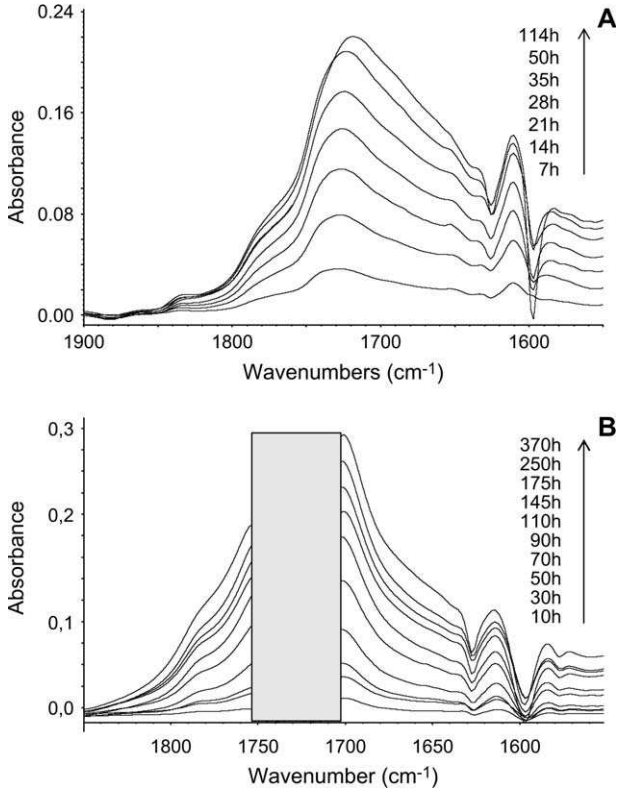


Fig. 3. Changes in the 1900–1500 cm^{-1} region of the IR spectra (subtraction between the irradiated and the non-irradiated sample) of PVK (A) and COP film (B) caused by photooxidation in the SEPAP 14.24 unit at 30 °C.

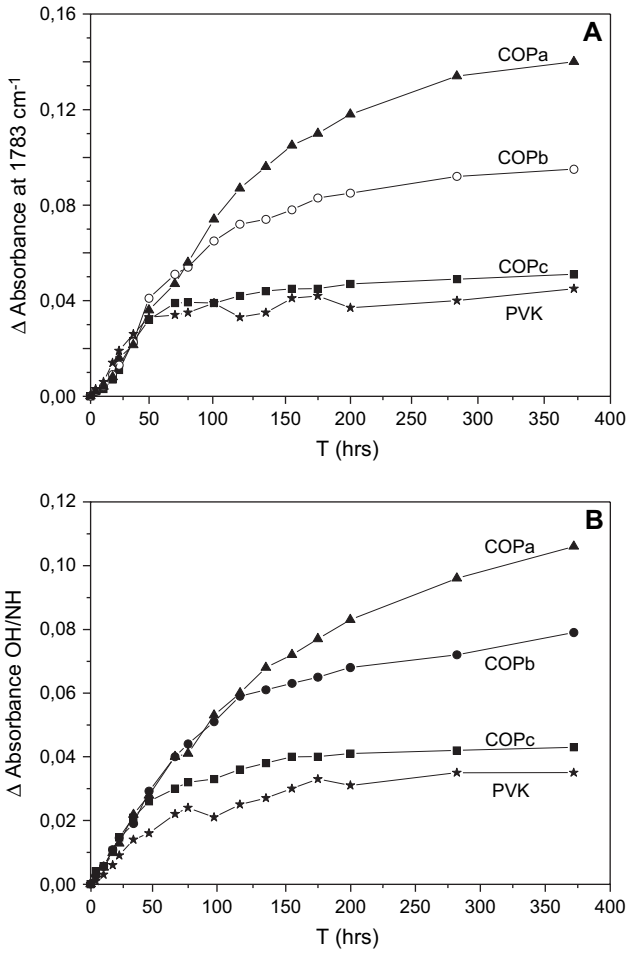


Fig. 4. Increase in the absorbance at 1783 cm^{-1} (A) and in the NH/OH region (B) for PVK and COP films as a function of irradiation time in the SEPAP 14.24 unit at 30 °C.

shoulder is formed around 1783 cm^{-1} and, as in PVK, a thin band develops at 1610 cm^{-1} whilst the intensity of the two ring vibrations of the polymer at 1626 and 1597 cm^{-1} decreases.

The increase of absorbance measured either at 1783 cm^{-1} or at the maximum of absorbance in the OH/NH region for PVK and copolymers is plotted in Fig. 4. These measurements, respectively, represent a priori an evaluation of the total carbonyl groups $(CO)_{tot}$ and OH/NH groups $(OH/NH)_{tot}$ formed in the polymers.

From the analysis of the curves drawn in Fig. 4, it can be concluded that, for a same amount of absorbed light, the photooxidation of copolymers involves two periods.

1. The photooxidation rates of the copolymers and PVK are similar in the first period of exposure (70 h) and the increase in absorbance is a linear function of the irradiation time. This result strongly suggests that the photodegradation is restricted to the carbazolyl moieties, which are responsible for the direct light absorption.
2. For longer exposures (>70 h), photooxidation appears to be more pronounced in copolymers than in PVK for which oxidation reaches an invariant state. This result would account for the involvement of a photo-induced oxidation of the CEM and OMA moieties: the propagation of the oxidative reactions to ether and ester moieties can be initiated by radicals obtained in the N–C bond scission.

The presence of different concentrations of CEM1, CEM2 and OMA moieties containing ester and ether groups, which do not absorb the incident light, affects the oxidation rate. The decreasing order related to the concentration of oxidative species – COPa > COPb > COPc – is the same as the one obtained in the photo-yellowing measurements. Surprisingly, the more the copolymer contains ether sites, these later being very sensitive to photooxidation [18], the less the copolymer is oxidised. The following points have to be taken into account to interpret this unexpected result:

1. Former results obtained in our laboratory have shown the high reactivity of polyethers to UV induced oxidation [19] and the oxidation of the polyether segments was shown to be very rapid in the case of copoly(ether–ester) [20].
2. It is worthy to recall that oxidation involves the carbon atom in α-position of the ether groups. Secondary hydroperoxides are formed and their main way of decomposition is a β-scission reaction leading to the formation of formates (1725 cm^{-1}). The primary alkyl radicals formed along with the formates are oxidised into carboxylic acids (1710–1717 cm^{-1}).

Conversely to polyethers, PMMA is relatively stable to photodegradation at long wavelengths ($\lambda > 300$ nm) [21]. The photooxidation of PMMA leads to the formation of alcohol groups (3550–3320 cm^{-1}) and esters (1735–1750 cm^{-1}).

Consequently, the measurement of the increase of absorbance at 1783 cm^{-1} is related to the degradation of the PVK unit in each copolymer. But the question remains open to know if it reflects the total carbonyl groups $(CO)_{tot}$ formed in copolymers. NH_3 treatments presented in the next section will suggest an answer to this question.

3. The photooxidative degradation can lead to significant formation of low molecular weight photoproducts that can migrate out of the polymer sample. The formation of low molecular weight photoproducts is more likely to occur in the case of polymers having short branched reactive groups [22]. Thus infrared analysis of the oxidative evolution of the solid sample does not permit recording the formation of all the photoproducts.

As a conclusion, all these data strongly suggest that the more the polymer contains short branched reactive CEM2 units, the less the oxidation rate measurements at 1783 cm^{-1} or in the OH/NH domain represent an evaluation of the whole oxidative species formed in the polymers. Indeed, these measurements underestimate the formation of photoproducts resulting from the oxidation of the ether sites.

3.2. NH_3 treatments of irradiated samples

NH_3 treatments were carried out on photooxidised PVK and COPb films irradiated for 70 h and 370 h. NH_3 reactions lead to a decrease in the carbonyl absorption region between 1800 and 1700 cm^{-1} and to the formation of maxima around 1660 and 1570 cm^{-1}. These maxima correspond, respectively, to amide and carboxylate ion bands obtained by reaction with NH_3 of esters and of carboxylic acids, respectively, observed around 1738 and 1713 cm^{-1} in PVK. It is worthy to recall that the development of these absorptions cannot be observed in copolymers due to the presence of the initial broad ester vibration. Results of NH_3 treatments of PVK and COPb films throughout irradiation are reported in Table 2. The absorbance at 1570 cm^{-1} produced after NH_3 treatment represents an evaluation of the carboxylic acid groups (COOH) formed throughout exposure.

Table 2
Changes of absorbance after irradiation (1783 cm^{-1}) and after NH_3 treatment (1570 cm^{-1})

Duration of exposure	70 h		370 h	
Absorbance	1783 cm^{-1}	1570 cm^{-1}	1783 cm^{-1}	1570 cm^{-1}
PVK	0.05	0.08	0.06	0.06
COPb	0.05	0.08	0.09	0.13
COPb/PVK	1	1	1.5	2.1
Carbonyl group	$(CO)_{tot}$	COOH	$(CO)_{tot}$	COOH

Results reported in Table 2 can be interpreted as follows:

- During the first 70 h of exposure both the increase of absorbance at 1783 cm^{-1} and the concentration of carboxylic acid are the same in PVK and COPb. This result suggests that the photodegradation is initially restricted to carbazolyl moieties, sites of light absorption.
- For longer exposure, the degradation of copolymer occurs at a higher rate than that of PVK and the accumulation of carboxylic acids is favoured in copolymer. Such a difference suggests that radical species formed in the degradation of the carbazolyl moieties are able to induce the oxidation of the CEM and OMA units. In addition, the identification of the carbonylated photoproducts by means of chemical treatments confirms the interpretations deduced from analysis of the IR spectra: the measurement of the absorbance at 1783 cm^{-1} underestimates the formation of oxidative species resulting from the oxidation of ether and ester units.

3.3. ESR analysis

PVK and COPb films (10 mg) have been irradiated at $\lambda > 350$ nm and analysed in situ by ESR spectroscopy either under argon atmosphere or at ambient air. In both cases, during the first 15–20 min of exposure, a singlet centred at 3440 G with a width of about 40 G is observed on the recorded spectra indicating an accumulation of free radicals (Fig. 5).

The intensity of the ESR signal has been plotted as a function of the exposure duration (Fig. 6).

The analysis of curves drawn in Fig. 6 allows to point out the following remarks:

- After the first period of 15–20 min of exposure, the radical concentration increases at a lower rate.
- The radical concentration is higher in PVK than in the case of COPb.
- The radical concentration is higher when irradiation is carried out at ambient air than under argon atmosphere.
- After UV exposure had been stopped (180 min), the ESR signal was recorded during 180 min. A rapid emission quenching is observed during the first 15–20 min and then the radicals concentration reaches a stationary value which is different from the initial value suggesting that several radical types are formed with different stabilities.

The presence of stable radical species may be related to the presence of carbazolyl units. The percentage of carbazole is about two times lower in COPb than in PVK, which explains why radicals are formed at higher concentration in PVK than in COPb.

3.4. Molecular weight changes upon irradiation

PVK and copolymers are initially soluble in tetrahydrofuran (THF) at room temperature. After irradiation an insoluble part

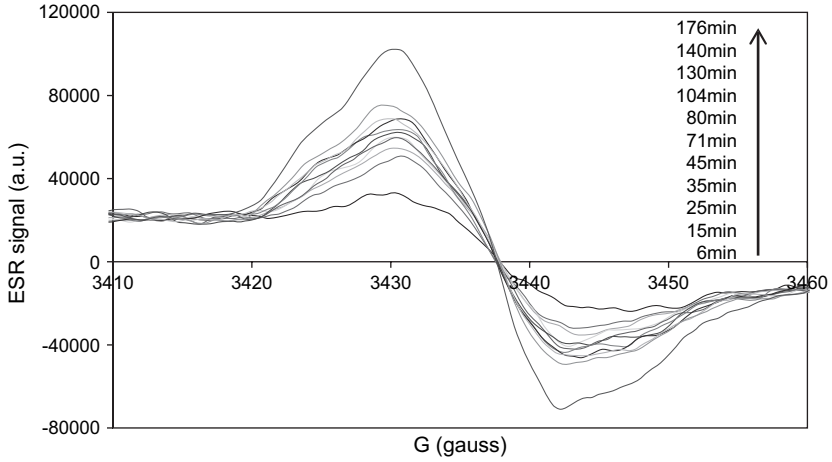


Fig. 5. ESR spectra of PVK films at different times of UV exposure ($\lambda > 350$ nm).

is produced. The amount of insoluble material was determined by gravimetric measurements. Results are reported in Fig. 7.

Crosslinking appears to be the major phenomenon occurring during the initial period of the irradiation of PVK and COPb films. For PVK, the amount of insoluble fraction increases to a higher extent during exposure than for COPb.

The evolution of the molecular weight (Mw) of the soluble fraction in THF of irradiated films was determined by SEC. Results are shown in Fig. 8.

The M_w of the soluble fraction of irradiated PVK and COPb films increases rapidly under exposure and reaches a maximum value within 30 min of irradiation in the case of PVK and 3 h in the case of COPb. Then an insoluble network is formed and M_w rapidly decreases, reaching a very low value: only oligomeric macromolecules remain soluble in THF.

As a conclusion, the analysis of results obtained from insoluble fraction and M_w measurements suggests that the rate and extent of crosslinking is higher in PVK than in COP. CEM and OMA spacers, for which the degradation involves chain scissions, may inhibit the formation of the three dimensional network in the copolymers.

3.5. Emission spectra

The comparison of the fluorescence emission of PVK and COPb necessitates that both polymers present the same absorbance at the excitation wavelength. The thickness of the films was chosen so that both polymers present the same absorbance of 0.3 at 340 nm. The fluorescence spectra of PVK and COPb were measured under excitation at 340 nm. In these conditions of excitation, the emission spectrum of COPb presents a main band at 365 nm with a shoulder around 355 nm (Fig. 9A) similar to carbazole monomer emission bands [14].

No excimer emission characterised by a maximum around 420 nm was observed. Such a result was previously observed with carbazole-containing copolymers and attributed to the fact that the flexibility of the linking groups does not favour the adoption of the parallel overlap inter-chromophore geometry necessary for excimer formation [14].

As previously observed with carbazole-containing methacrylate polymers [14], the exposure of COPb induces a rapid total disappearance of the fluorescence of the irradiated film.

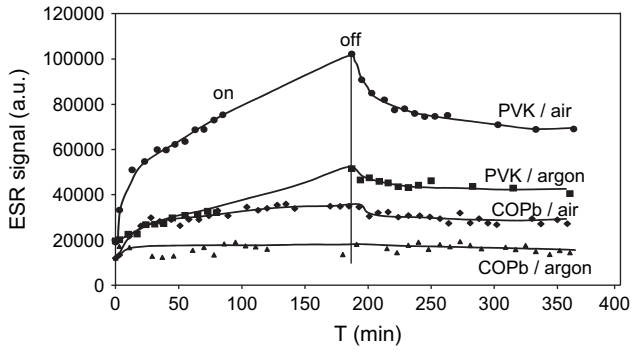


Fig. 6. Changes in the intensity of the ESR signal of PVK and COPb as a function of UV exposure ($\lambda > 350$ nm) at ambient air or under argon atmosphere.

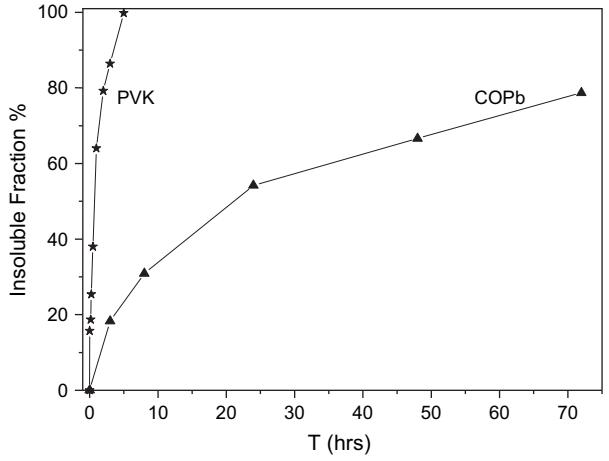


Fig. 7. Determination of the insoluble fraction of PVK and COPb films as a function of irradiation time in the SEPAP 14.24 unit at 30 °C.

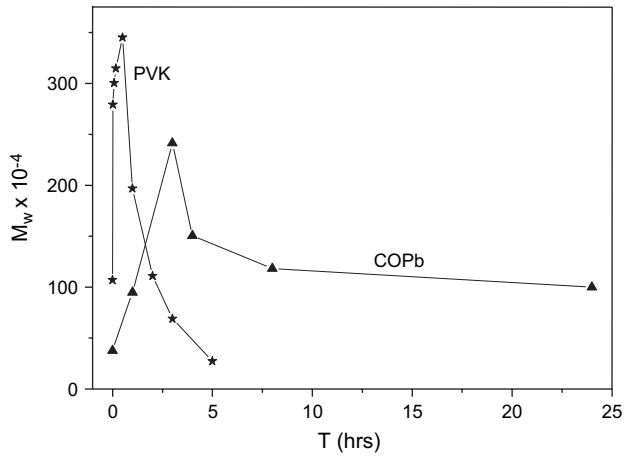


Fig. 8. Evolution of *M*w of PVK and COPb films as a function of irradiation time in the SEPAP 14.24 unit at 30 °C.

The results given in Fig. 9B show that a 50% decrease of the monomer fluorescence intensity is achieved after 5 min of COPb exposure and the total disappearance is obtained after about 20 h. This disappearance cannot be directly compared to the decrease of the excimer fluorescence of PVK, which is a consequence of the decrease of the local mobility resulting from crosslinking [9].

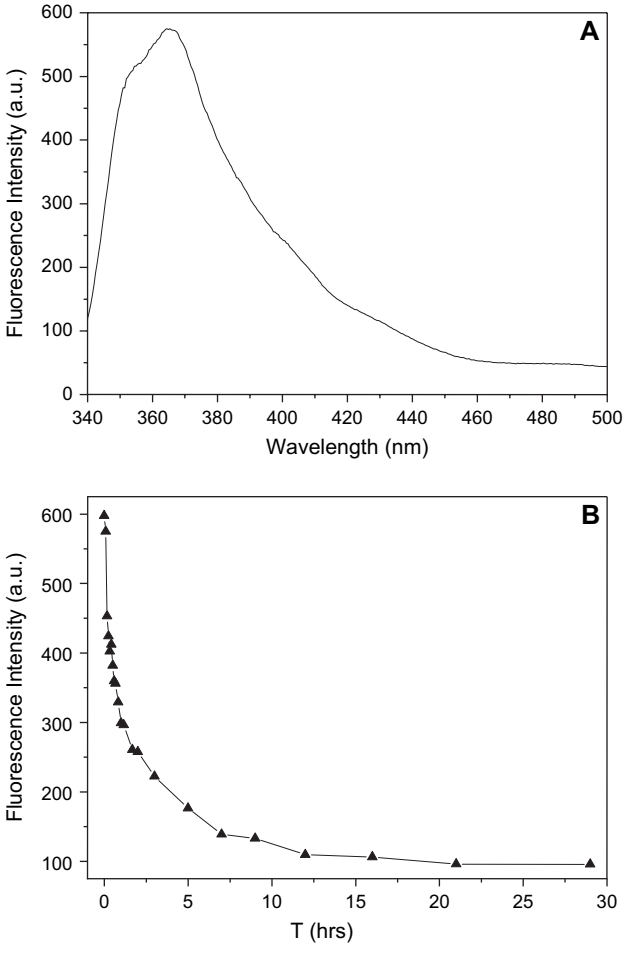


Fig. 9. Emission spectrum of COPb under excitation at 340 nm (A) and changes in the fluorescence intensity of COPb (B) as a function of irradiation time in the SEPAP 14.24 unit at 30 °C.

4. Conclusions

These first investigations on the photodegradation processes of carbazole-containing copolymers show that, in conditions of irradiation at long wavelengths, the absorption of light is controlled by the carbazolyl moieties. The photodegradation, resulting from the scission of the N–C bond, is initially restricted to these carbazolyl moieties. It involves radical species that induce the oxidation of the CAM and OMA components for longer irradiation durations.

The phototransformation of copolymer, as previously observed for PVK, is principally governed by crosslinking reactions. Spacing the carbazolic units by CEM and OMA moieties reduces the progression of the three dimensional network in copolymers.

References

[1] Klöpffer W. Chem Phys Lett 1969;4(4):193.
[2] (a) Itaya A, Okamoto K, Kusabayashi S. Bull Chem Soc Jap 1976; 49(8):2082;
(b) Itaya A, Okamoto K, Kusabayashi S. Bull Chem Soc Jap 1977; 50(1):22;
(c) Itaya A, Okamoto K, Kusabayashi S. Bull Chem Soc Jap 1979; 52(8):2218.
[3] Johnson GE. J Chem Phys 1975;62(15):4697.
[4] Hoyle CE, Nemzek TL, Mar A, Guillet JE. Macromolecules 1978; 11(2):429.
[5] (a) Ghiggino KP, Wright RD, Phillips D. Eur Polym J 1978;14:567;
(b) Ghiggino KP, Archibald DA, Thistlethwaite PJ. J Polym Sci Polym Lett Ed 1980;18:673.
[6] (a) De Schryver FC, Vandendriessche J, Toppet S, De Meyer K, Boens N. Macromolecules 1982;15:406;
(b) Vandendriessche J, De Schryver FC. Polym Photochem 1986;7:153.
[7] Pfister G, Williams DJ. J Chem Phys 1974;61(6):2416.
[8] Itaya A, Sakai H, Masuhara H. Chem Phys Lett 1987;138(2,3):231.
[9] Rivaton A, Mailhot B, Derderian G, Bussiere PO, Gardette JL. Macromolecules 2003;36:5815.
[10] Ranby B, Rabek JF. Photodegradation, photooxidation and photostabilization of polymers. London: Wiley; 1975.
[11] Sanetra J, Bogdal D, Niziol S, Armatys P, Pielichowski J. Synth Metals 2001;201:1731.
[12] Robu S, Bivol V, Dragalina G, Vlad L, Bolte M, Chapurin I. Polym Mater Sci Eng 2001;85:337.
[13] Davidson K, Soutar I, Swanson L, Yin J. High Perform Polym 1997; 9:353.
[14] Keyanpoor-Rad M, Ledwith A, Hallam H, North AM, Breton C, Hoyle C, et al. Macromolecules 1978;11:1114.
[15] Robu S, Mailhot B, Dragalina G, Vlad L, Pilichowski JF, Bolte M, in preparation.
[16] Carlsson DJ, Brousseau R, Zhang C, Wiles DM. ACS Symp Ser 1988; 364:376.
[17] Wilhelm C, Gardette JL. J Appl Polym Sci 1994;51:1411.
[18] Gardette JL, Posada F, Philippart JL, Kappler P. Macromol Symp 1997; 115:53.
[19] Morlat S, Gardette JL. Polymer 2001;42:6071.
[20] Tabankia MH, Philippart JL, Gardette JL. Polym Degrad Stab 1985; 12:349.
[21] Siampiringue N, Leca JP, Lemaire J. Eur Polym J 1991;27:633.
[22] Pholippart JL, Posada F, Gardette JL. Polym Degrad Stab 1995;49:285.